

PHYSICAL MODES OF THIN-FILM PV DEGRADATION

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ABSTRACT

We discuss physical modes of degradation related to the small thickness and lack of crystallinity in thin-film PV. We discriminate between 1) uniform material degradation through defect generation, light-induced diffusion, and electro-migration; 2) nonuniform degradation through ohmic or non-ohmic shunts; 3) metal contact deterioration. The first can equally apply to bulk and thin-film PV. Two others are specific to thin-film PV.

INTRODUCTION

Stability remains a major issue in thin-film PV technology. Several degradation mechanisms have been discussed in terms of either physical processes (electromigration, diffusion, defect generation) or chemical reactions [1], assuming a uniform structure similar to the bulk crystalline devices. In the mean time, it is commonly recognized that thin-film PV exhibit degradation patterns different from their crystalline counterparts. This suggests that the small film thickness and lack of crystallinity are important stability factors. Both are conducive to lateral nonuniformities [2], hence, nonuniform degradation, such as shunting. In addition, the film rough surfaces can result in metal contact problems as discussed in what follows.

SHUNTING PHENOMENA

Shunting instability

A simple argument showing how the small film thickness promotes shunting is based on the system energy analysis. It takes into account a capacitive energy W_C stored in the film under external bias U . This energy discharge can cause a local atomic rearrangement in the form of a conductive path (shunt) across the device. We call this scenario shunting instability. Structural defects or impurity atoms forming chain-like configurations (Fig. 1a) can be shunting precursors underlying the instability.

The discharge becomes possible due to the film small thickness l and correspondingly large capacitance C , which makes the energy $W_C = CU^2/2$ rather high. In particular, W_C can exceed the energy $W_D = N_l w$ needed to create a large number $N_l \sim l/a$ of defects

forming a shunt. Here a is the defect linear dimension, and w is the defect generation energy.

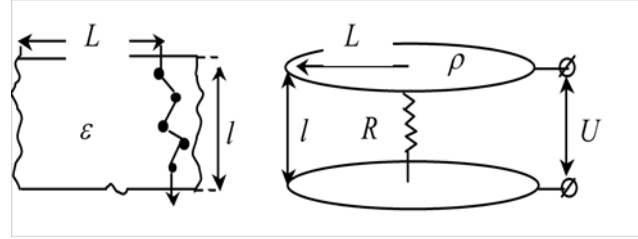


Fig. 1. Sketch of an N-defect shunting chain through a thin film and its equivalent electric circuit.

The inequality $W_C \gg W_D$ obeys for surprisingly low $U \sim 1$ mV. To estimate W_C we use $C = \epsilon A / 4\pi l$ with $A = \pi L^2$ corresponding to a cylindrical capacitor whose radius is equal to the characteristic length over which a shunt affects the electric potential distribution [2], $L = \sqrt{kT / q\rho J_{SC}}$. Here kT is the thermal energy, q is the electron charge, ρ is the TCO sheet resistance, and J_{SC} is the short-circuit current density. Under 1 sun illumination, L is typically of the order of several millimeters. A thin-film structure is then represented by a capacitor with a linear dimension L of several millimeters and a micron size gap l . As a result, the ratio of the above two energies,

$$\xi \equiv W_C / W_D = \epsilon L^2 a U^2 / 8 l^2 w \quad (1)$$

becomes very large. Putting the typical $L = 3$ mm, $l = 3$ μ m, $\epsilon = 10$, $a = 1$ nm, $U = 1$ V, and $w = 1$ eV, yields $\xi \approx 10^6$. To emphasize the significance of this result, we note that $\xi \sim 1$ for $U \sim 1$ mV, that is a micron thick structure is unstable with respect to shunting already in the mV range.

Shunt nucleation

The latter instability is of a thermodynamic nature and takes extremely long time to occur. It can be shown that the transition from a non-shunted to a shunted state occurs as a nucleation event similar to the first-order phase transition [3]. A shunting nucleus appears as a poorly conducting defect chain. It changes the electric potential difference across the device and thus decreases its capacitive energy. While relatively small, the latter

decrease can still be significant as compared to W_D , which makes the nucleation energetically favorable.

Shunt nucleation possesses all the standard nucleation kinetics features: critical embryo (shunt) and corresponding nucleation barrier, sub-critical shunts that stochastically appear and disappear in the system, super-critical shunts irreversibly growing to become permanent, extremely high sensitivity to structural and compositional fluctuations, and random nature of nucleation events.

Such a nucleation type of shunting scenario for CdTe devices was apparently observed in Refs. [4,5]. Its theoretical description [3] based on accounting for the tunneling resistance $R = R_0 \exp(2l / Na)$ of an N-defect shunting path, yields the shunting probability

$$p = \nu \exp(-wl/kTa\Lambda), \quad \Lambda \equiv \ln(\xi R_0 / \rho) \gg 1 \quad (2)$$

where ν ($\sim 10^{13} \text{ s}^{-1}$) is of the order of the characteristic atomic frequency, and $R_0 \sim 1 \text{ M}\Omega$.

In many cases, mobile impurities form conductive paths more easily than structural defects. This can be described by the above theory where the defect generation energy is replaced by the minimum work (per impurity atom) needed to form the path. As expressed through the system entropy, $w = kT \ln(N_i / \langle N \rangle)$ where

$\langle N \rangle$ is the average number of impurity atoms in a critical shunt volume ($\sim l^3$). Because of $w \propto T$, this mechanism leads to a temperature independent exponential in Eq. (2). In the mean time, the pre-exponential represents the temperature activated impurity diffusion frequency.

The above nucleation analysis implied laterally uniform structures. In reality, heterogeneous nucleation of conductive paths can dominate the shunting kinetics in non-crystalline thin-film PV. This brings about nucleation features characteristic of random systems [6], such as exponential increase in nucleation probability and a parabolic Arrhenius plot for nucleation rate vs. T [3], but does not entail qualitative changes in the above picture.

Specific predictions

It is typical that defects and impurity atoms accumulate towards the device edges. In the above terms, this points at higher $\langle N \rangle$, lower w , and predicts shunting to be stronger in the edge region, which is consistent with the recent observations on thin-film photovoltaics [7].

One other verifiable prediction is that because of their underlying hopping transport, the shunts should be highly non-ohmic. We have verified this by purposely creating shunts under significant reverse bias, (of several Volts, varying between individual cells). Under ambient room light, the JV curves of the original and shunted cells in Fig. 2 show indeed strong non-ohmicity: the difference between short-circuit currents is relatively small, while the reverse current of a shunted cell is exponentially higher. We have also verified that a shunt is a localized entity by cutting the shunted cell into two halves, one of which

retained the original (non-shunted) characteristics, while another one appeared as shunted as the entire cell.

For a particular case of CdS/CdTe PV, the above scenario suggests a possibility of CdS layer shunting by Cu atoms forming conductive paths. It is known indeed that Cu accumulates in CdS [8] and that shunting through CdS can appear as though the entire cell was shunted [9]. Assuming this mechanism, the CdS morphology can be an

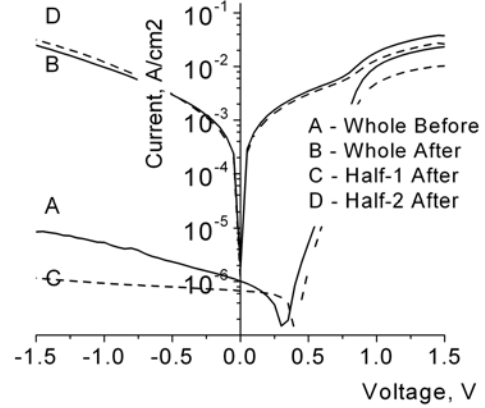


Fig. 2. JV characteristics of a CdTe solar cell and its two halves before and after shunting. Note the log scale and that the reverse current is shown in absolute value. Non-shunted sample JVs show a kink at the open circuit voltage that is relatively high under an ambient light of low intensity.

important factor determining the shunt nucleation rate. It also explains how in some cases Cu can be detrimental to the device stability, while in other cases Cu doped samples remain stable.

Finally, our theory predicts a possibility of suppressing shunt nucleation by adding a proper interfacial layer. Because it exponentially increases the N-defect chain resistance R , such a layer will strongly suppress the probability of shunt nucleation.

CONTACT DETERIORATION

There is ample evidence of contact related PV degradation. Here we discuss the physical mechanisms that can lead to contact problems, particularly, metal delamination under light soak. Our scenario is based on the concept of bias dependent adhesion, according to which, a light induced bias changes the metal adhesion. On a rough surface, this can result in small scale delamination spots [10], and cause several detrimental effects: increase in series resistance (R_s), decrease in fill factor and open-circuit voltage (V_{oc}), and thermal instability leading to electric breakdown.

Bias dependent adhesion

The oppositely charged metal and semiconductor attract, contributing to the adhesion. Under external bias, their electric charges change causing the corresponding

change in adhesion. Such bias dependent adhesion was observed for some systems [11].

When the interface is rough, as it typically is for polycrystalline semiconductors (Fig. 3a), the change in adhesion will induce local stresses (Fig. 3b) leading to the metal film deformation. As a result, the metal contact can deteriorate under external bias, in particular, light-induced bias in PV. A decrease in metal adhesion after light soak was indeed observed [12].

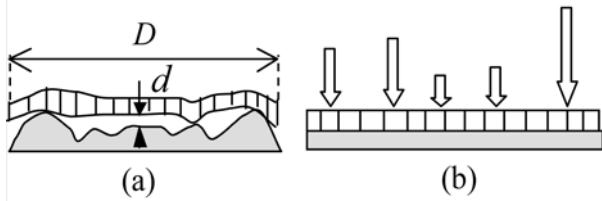


Fig. 3. Sketch of a thin metal film on a rough surface in micron (a) and millimeter (b) scale. Fat arrows show the electrostatic pressure distribution.

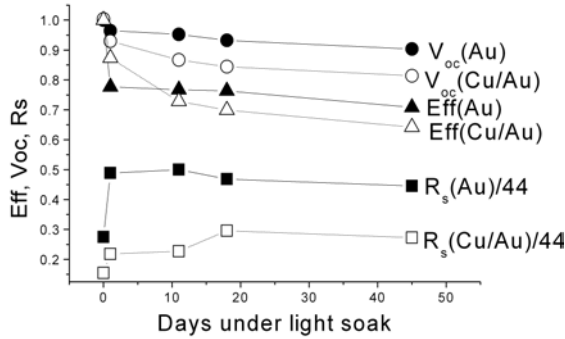


Fig. 4. Light soak induced degradation of a Cu free device with a cold evaporated Au contact vs. the standard Cu/Au annealed back contact for the open circuit voltage Voc and efficiency normalized to their initial values, and conveniently rescaled series resistance Rs/44 (Ohm).

We assume that certain (metal dependent) degree of non-conformational growth results in a multitude of microscopic voids between the metal film and semiconductor surface. Similar to the parallel plate capacitor, this creates the electrostatic pressure

$$p = \epsilon V^2 / 8\pi d^2, \quad (3)$$

especially high for narrow gap d (Fig. 3a). The electric potential difference V between the metal and semiconductor is due to the fact that a delaminated spot is electrically disconnected and thus generates surface photovoltage, which is higher than the voltage under working conditions in the rest of metallized device. Assuming as a rough guide $V \sim 1$ V and $d \sim 1$ nm gives $p \sim 100$ atm. Taking into account variations in d , local pressure will fluctuate in the range of up to ~ 100 atm along the metal film (Fig. 3b). The corresponding strain

can be estimated as [13] $\zeta \sim (p/Y)(D/h)^3 \leq 0.1$ where Y and h are respectively the metal film Young's modulus and thickness. It can be significant enough to promote further delamination, loss in adhesion, and drop in device performance.

Our data for CdTe PV (Fig.4) show indeed the initial efficiency drop correlated with a drastic increase in series resistance that we attribute to contact delamination. The magnitude of this effect depends on the back contact recipe: it is stronger for Au cold evaporated contacts as compared to the standard Cu/Au recipe followed by anneal. The subsequent evolution shows a superior stability of Cu free devices, similar to the data of Ref. [14] and consistent with the known role of Cu as a source of CdTe device instability.

Thermo-Electric Instability

Delaminated micro-spots can become a source of potential electric breakdown. This happens when the lateral electric current in a delaminated spot generates enough heat to significantly decrease the semiconductor resistance. In its turn, this will increase the current, generate more heat, etc. - similar to the chain reaction instability. As a result, the local temperature can rise up to trigger the device electric breakdown.

The above scenario is described by the equation of thermal conduction and Ohm's law

$$\chi \nabla^2 T = -\sigma E^2, \quad \sigma = \sigma_0 \exp(-\Delta/kT). \quad (4)$$

Here E is the electric field, χ and σ are the thermal and activated electric conductivity. We impose the boundary condition that the temperature is fixed (T_0) at the metal film and estimate $E = V/D$ where D is the lateral dimension of a delaminated spot (see Fig. 3a).

Analyzing Eq. (4) similar to the known chain reaction technique [15], yields a dimensionless parameter

$$\lambda = \sigma V^2 d^2 \Delta / \chi k T^2 D^2, \quad (5)$$

such that the instability occurs when $\lambda > 1$. The latter inequality can take place for the typical thin-film PV parameters.

Delamination spots conducive to thermo-electric instability can as well originate from several extraneous factors, such as, for example, mechanical stress, or water intrusion in combination with a rough surface.

Interfacial layer (IFL) effects

Putting an IFL between the metal and semiconductor will have two strong effects on the system. First, it increases the gap d and thus reduces the local pressure variations [see Eq. (3)]. Secondly, it provides a certain cushion that mitigates stresses in the metal film. Our data in Fig. 5 show indeed that an IFL significantly decreases the back contact related problems (usually observed in the

first days of light soak; cf. Fig. 4) as compared to the no-IFL samples. Here we used Cu free CdTe PV with Au back contact described in Ref. [9], and aniline based IFL described in Ref. [16].

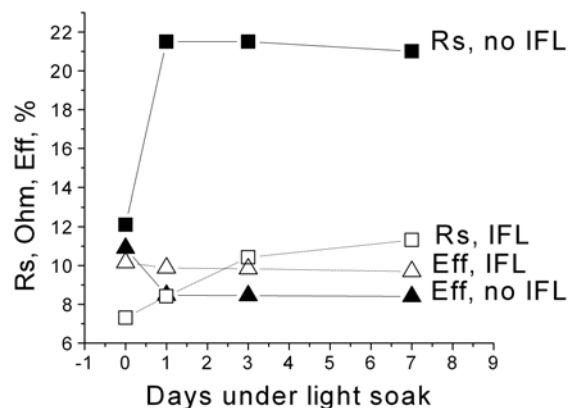


Fig. 5. Degradation of series resistance and efficiency for Cu-free CdS/CdTe samples with Au cold evaporated back contact with and without IFL.

CONCLUDING REMARKS

We have discussed two physical mechanisms of degradation specific to thin-film PV: shunting and metal contact delamination. They have more bearing upon the device structure and its inherent nonuniformity than on the underlying material chemistry, and can be common to different types of thin-film PV.

Both mechanisms predict significant positive effects of IFL. Indirectly, this also points to minute (in some cases, unintentional) surface modifications affecting the device stability, such as season dependent ambient atmosphere, light intensity, etc.

The above philosophy of thin-film specific degradation calls for discriminating between the material and structure related degradation mechanisms. Properly identifying the nature of degradation will help to adequately direct future efforts in improving the device stability. For example, if the material degradation prevails, then the nature of structural defects and doping become crucial. If, however, the structure specific mechanisms are more important, then more attention should be paid to the contact related issues, use of IFL, lateral uniformity, etc.

In some cases, there is evidence of structure related mechanisms prevailing. For example, CdTe is generally known for its high radiation stability (used in X-ray detectors). In spite of this, some of CdTe based PV show rather poor device stability under light soak, while others, chemically similar structures are quite robust.

In conclusion, we would like to point at two diagnostics capable of at least partially discriminating between the material and structure degradation. One is a comparison between the surface photovoltage (SPV) and Voc. As opposed to Voc, the SPV is measured on a non-metallized surface, less affected by lateral nonuniformities, surface roughness, etc., and characterizes rather the main junction (material) degradation. The second is a

comparison between PL intensity in the metallized and non-metallized regions, which, from our preliminary results, degrade differently, with the implications similar to those of Voc vs. SPV comparison.

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